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FLAVONOID ACYL GLYCOSIDES OF GRATIOLA OFFICINALIS

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In the separation of the total flavonoids from Gratiola officinalis L., in addition to C-glycosides we obtained two O-glycosides.

The first of them, which we have called lignoside, had mp 245–247° C, $[\alpha]_D^{20}$ −91.6° (c 0.103; dimethylformamide), R_f in system 1 (15% acetic acid) 0.38, in system 2 [butan-1-ol–acetic acid–water (4 : 1 : 2)] 0.48; $\lambda_{max}^{C_2H_5OH}$ 330 (plateau), 318, 278 mμ; $E_{1cm}^{1\%}$ 320, 370, 290 respectively; $\lambda_{max}^{C_2H_5OH+AcNa}$ 326 (plateau), 310, 278 mμ; $\lambda_{max}^{C_2H_5OH+C_2H_5ONa}$ 385, 276 mμ, $\lambda_{max}^{C_2H_5OH+Zr(NO_3)_2}$ 335, 320, 280 mμ.

The second, which we have called isolignoside, had mp 230–232° C; $[\alpha]_D^{20}$ −147.3° (c 0.038; dimethylformamide); R_f in system 1, 0.28; in system 2, 0.38; $\lambda_{max}^{C_2H_5OH}$ 340, 310, 278 mμ; $E_{1cm}^{1\%}$ 460, 335, 380 respectively. $\lambda_{max}^{C_2H_5OH+AcNa}$ 375, 310, 270 mμ; $\lambda_{max}^{C_2H_5OH+C_2H_5ONa}$ 370, 290 mμ; $\lambda_{max}^{C_2H_5OH+Zr(NO_3)_2}$ 425, 320, 280 mμ. On chromatograms, both glycosides gave dark spots the color of which changed little under the action of zirconyl nitrate and ammonia vapor, which is characteristic for scutellarein derivatives.

The IR spectra of both glycosides exhibited, in addition to frequencies characteristic for flavonoid glycosides, a band at 1715 cm^{-1} due to an ester grouping [1].

Acid hydrolysis yielded D-glucose and aglycones which have been named lignogenin with R_f 0.72 in system 3 (benzene–ethyl acetate–acetic acid (30 : 70 : 2)) $\lambda_{max}^{C_2H_5OH}$ 335, 305, 280 mμ; $\lambda_{max}^{C_2H_5OH+AcNa}$ 335, 305, 280 mμ; $\lambda_{max}^{C_2H_5OH+C_2H_5ONa}$ 380, 335, 285,mμ; $\lambda_{max}^{C_2H_5OH+Zr(NO_3)_2}$ 370, 285 mμ, and isolignogenin with R_f 0.45 in system 3, $\lambda_{max}^{C_2H_5OH}$ 335, 310, 280 mμ; $\lambda_{max}^{C_2H_5OH+AcNa}$ 335, 285 mμ; $\lambda_{max}^{C_2H_5OH+C_2H_5ONa}$ 385, 290, 275 mμ; $\lambda_{max}^{C_2H_5OH+Zr(NO_3)_2}$ 380, 290, 280 mμ.

The ratio of the specific intensities of the long-wave maxima of the glycosides to their aglycones, which is between 50 and 60%, characterizes them as monoglycosides.

On acid treatment, the aglycones of these glycosides underwent anhydridization with the formation of new compounds, and further acid hydrolysis in a mixture of concentrated H_2SO_4 and glacial CH_3COOH led to the splitting off of a substituent which is probably in the 4' position. The alkaline cleavage of the aglycones gave mainly p-hydroxybenzoic acid, while the cleavage of their anhydro form gave vanillic acid.

In view of the proportion of substituent from the percentage ratio (about 60%) of the intensities of the long-wave maxima to their 4'-dealkylated forms, and also taking into consideration the products of alkaline cleavage, it may be assumed that lignoside and isolignoside are alkylated in the 4' position with 1,2-dihydroxydihydroconiferyl alcohol.

From the features of the UV spectra and the bathochromic shifts of the zirconyl complexes of the glycosides and aglycones it follows that in lignoside the $C_{(6)}$ hydroxyl group is substituted by a sugar residue while in isolignoside this position is free and the carbohydrate substituent is apparently at $C_{(8)}$. The hydroxy group at $C_{(7)}$ in these glycosides is methoxylated, and only that at $C_{(5)}$ is free. The dealkylation of the aglycones of lignoside led to the production of scutellarein, and that of the aglycones of isolignoside to isoscutellarein. Neither of the monoglucosides was cleaved by emulsin, and on hydroxylaminolysis [2, 3] acethydroxamic acid was formed. On this basis, it may be assumed that the acyl group is an acetic acid residue and it is located in the carbohydrate part.

Thus, the new flavonoid glycosides of Gratiola officinalis are acylated derivatives and belong to a new class which may be called semilignane flavones.

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